

Role of electronic correlations in the Fermi surface formation of Na_xCoO_2

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Band structure of metallic sodium cobaltate Na_xCO_2 ($x=0.33, 0.48, 0.61, 0.72$) has been investigated by local density approximation+Hubbard U (LDA+ U) method and within Gutzwiller approximation for the $\text{Co-}t_{2g}$ manifold. Correlation effects being taken into account results in suppression of the e'_g hole pockets at the Fermi surface in agreement with recent angle-resolved photo-emission spectroscopy (ARPES) experiments. In the Gutzwiller approximation the bilayer splitting is significantly reduced due to the correlation effects. The formation of high spin (HS) state in Co d -shell was shown to be very improbable.

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Introduction. Puzzling properties of sodium cobaltate Na_xCO_2 are the topic of many recent theoretical and experimental investigations. This material holds much promise for thermoelectronics due to its large thermopower¹ together with the relatively low resistivity². The discovery of superconductivity with T_c about 5K in $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ ² revived the interest in lamellar sodium cobaltates. Moreover, the charge and magnetic long range orders on the frustrated triangular lattice of cobaltate is of the fundamental interest. The band theory predict the complicated Fermi surface (FS) with one large hole pocket around the $\Gamma = (0, 0, 0)$ point and six small pockets near the $K = (0, \frac{4\pi}{3}, 0)$ points of the hexagonal Brillouin zone at least for $x < 0.5$ ^{3,4}. However, intensive investigations by several ARPES groups reveal absence of six small pockets in both $\text{Na}_x\text{CO}_2 \cdot y\text{H}_2\text{O}$ and in its parent compound Na_xCO_2 ^{5,6,7,8,9}.

The disagreement between ARPES spectra and *ab-initio* calculated band structure points to the importance of the electronic correlations in these oxides. Other evidences for the correlated behavior come from the data on an anomalous Hall effect and a drop of the thermopower in holistic magnetic field¹⁰.

The six hole pockets are absent in the L(S)DA+ U calculations^{12,13}. However, in this approach, the insulating gap is formed by a splitting of the local single-electron states due to spin-polarization, resulting in a spin polarized Fermi surface with an area twice as large as that observed through ARPES. Moreover, the long range ferromagnetic order has been set by hand because of limitation of LDA+ U . The predicted large local magnetic moments as well as the splitting of bands can be considered as artifacts of the L(S)DA+ U method.

Although LDA+ U method is usually applied to describe insulators, there are some achievement in investigation of metals and metallic compounds^{14,15}. To analyze the effect of electronic correlations on the Fermi surface formation in sodium cobaltate we employ both LDA+ U method and a Gutzwiller approximation.

Co d -level splits by crystal field of oxygen octahedron in lower t_{2g} and higher e_g bands. The deficiency of Na in Na_xCO_2 introduces additional holes in the system. Cobalt, having d^6 configuration and filled t_{2g} shell in parent NaCO_2 , is nonmagnetic. But in nonstoichiometric compound part of Co ions become magnetic with local moment about $1\mu_B$. This value is provided by d^5 configuration and one hole in t_{2g} shell. However, the experiments revealed the magnetic susceptibility at room temperature that is much higher than it was expected for dilute magnetic impurity in non-magnetic solvent. Explanation of this anomaly was suggested in Ref¹¹ as transition from low-spin (LS) state with six d -electrons on t_{2g} shell to high-spin (HS) state with five d -electrons on t_{2g} shell and one electron on e_g . The possibility of such transition will be discussed below.

LDA+ U results. $\text{Na}_{0.61}\text{CoO}_2$ crystallize in the hexagonal unit cell ($P6_3/mmc$ space group) with $a=2.83176(3)\text{\AA}$ and $c=10.8431(2)\text{\AA}$ at 12 K Ref¹⁸. Displacement of Na atoms from their ideal sites $2d$ ($1/3, 2/3, 3/4$) on about 0.2\AA are observed in nonstoichiometric cobaltates for both room and low temperatures. This is probably due to the repulsion of a randomly distributed Na atoms, locally violating hexagonal symmetry¹⁸. In the present investigation Na atoms are shifted back to their $2d$ ideal sites. In order to avoid charge disproportionation which can arises from some Na distribution if the supercell is used in calculation the change in the Na concentration has been considered in virtual crystal approximation (VCA) where each $2d$ site is occupied by virtual atoms with fractional number of valence electrons x and a core charge $11 - x$ instead of Na. Note, that all core states of virtual atom are left unchanged and corresponds to Na ones. We have chosen $4s$, $4p$, and $3d$ states of cobalt, $2s$, $2p$, and $3d$ states of oxygen, and $3s$, $3p$, and $3d$ states of Na as the valence states for TB-LMTO-ASA computation scheme. The radii of atomic spheres where 1.99 a.u. for Co, 1.61 a.u. for oxygen, and 2.68 a.u. for Na. Two classes of empty spheres

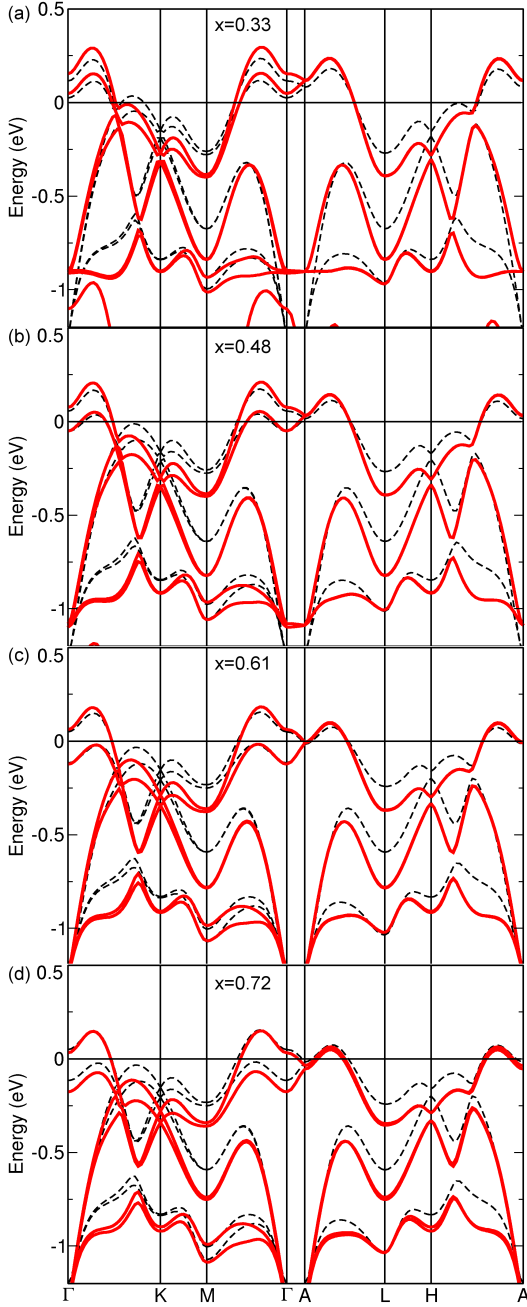


FIG. 1: (Color online) Band structure of Na_xCoO_2 for x equal to 0.33 (a), 0.48 (b), 0.61 (c), and 0.72 (d), obtained within LDA is shown by the black (dashed) curves. Band structures for the same doping concentrations within LDA+U are shown by the red (solid) curves.

(pseudo-atoms without core states) were added to fill the unit cell volume.

Crystal field of oxygen octahedron splits Co d -band into 2-times degenerate e_g and 3-times degenerate t_{2g} subbands (without taking into account spin). LDA calculations shows that those manifolds are separated on about 2 eV³. Here partially filled t_{2g} subband crosses the Fermi level whereas e_g subband due to strongly hy-

bridization with nearest oxygen atoms is positioned well above the Fermi level. The procedure proposed in Ref.¹⁹ allows one to calculate Coulomb repulsion parameter U taking into account the screening of localized d -shell by itinerant s - and p -electrons. Resulting U is equal to 6.7 eV. However, the presence of the t_{2g} - e_g splitting give the reason to take into account an additional screening channel provided by the less localized e_g electrons. The value of U for t_{2g} orbitals calculated using “constrained LDA” method²⁰, in which the screening by e_g electrons is also taken into account is equal to $U=2.67$ eV. The later value was used in the present calculation for all doping concentrations x . Hund’s exchange parameter J depends weakly on screening effects due to its “on-site” character. Its value was calculated within “constrained LDA” method and is equal to 1.07 eV.

First, we have verified the possibility of HS state formation on Co d -shell. For this purpose the unit cell of $\text{Na}_{0.61}\text{CoO}_2$ with two Co atoms was considered. We have started from a saturated A-type antiferromagnetic configuration with five electrons on the t_{2g} and one on the e_g shells. Small $U=2.67$ eV does not stabilize such magnetic configuration and LS state was obtained. Increasing U up to 5 eV however results in HS state with large local magnetic moment about $1.96 \mu_B$. Nevertheless, this HS state has the total energy about 1.75 eV higher then the energy of a LS state. This large difference in total energy of both considered spin states arises from hexagonal structure of cobaltates where the angle of Co-O-Co bond is close to 90° in contrast to almost 180° for, e.g., RCoO_3 ($\text{R}=\text{La}, \text{Ho}$). In the later case the e_g band has the width about 3-5 eV and its bottom lies just above the Fermi level. The system wins energy of $2J$ forming a HS state overcoming the gap energy which is less than 1 eV. Due to this fact difference between LS and intermediate spin states in RCoO_3 is less than 250 meV²¹. The angle of Co-O-Co bond is close to 90° in cobaltates and results in a weak overlap between e_g orbitals and hence in a narrow e_g band with larger gap between it and the t_{2g} band. Our calculation confirms that formation of HS in Na_xCoO_2 is rather improbable and cannot be stabilized by any distortion of crystal structure or clusterization proposed in Ref.¹¹. Local magnetic moments on Co sites can arise only due to holes doping due to Na atoms deficiency. Those holes order on Co atoms and form nonmagnetic Co^{3+} and magnetic Co^{4+} ions with d^6 and d^5 configurations, respectively. In the further calculations only the LS state was considered.

The ordering of holes on t_{2g} shell and corresponding long-range magnetic and charge order for $\text{Na}_{0.5}\text{CoO}_2$ arise probably due to specific arrangement of Na atoms. This arrangements were observed experimentally²² for several doping concentrations including $x = 0.5$. Proper description of such order within “unrestricted Hartree-Fock” gives strong spin and orbital polarization and local magnetic moment of about $1\mu_B$ on Co^{4+} sites as well as insulating ground state with sizable gap. To describe non-ordered systems the implementation of “re-

stricted Hartree-Fock" method is more suitable. In the later starting from non-magnetic configuration of d -shell with equal number of spin-up and spin-down electrons LDA+ U method gives non-magnetic solution without spin or orbital polarization. Note, that the gap does not open and Na_xCoO_2 remains metallic for all Na concentration.

Obtained band structure of Na_xCoO_2 for $x=0.33, 0.48, 0.61$, and 0.72 are shown in Fig. 1. Dashed (black) lines correspond to LDA results whereas solid (red) lines are the bands obtained by LDA+ U method. Cobalt d and oxygen p states are separated by a small gap of about -1.25 eV for $x=0.61$ and $x=0.72$. However, this gap disappears for lower doping concentration since the d band goes down when the number of d electrons decreases. The presence of the two CoO_2 layers within a unit cell due to alternation of the oxygen arrangement results in a bonding-antibonding (bilayer) splitting, also present in Fig. 1.

The degeneracy of the t_{2g} levels is partially lifted by the trigonal crystal field distortion which splits the former into the higher lying a_{1g} singlet and the lower two e'_g states. However, slight difference in occupation numbers of a_{1g} and e'_g orbitals (0.714 and 0.886 respectively for $x=0.33$) results in significant difference in LDA+ U band structure in respect to LDA one. The energy of the less occupied a_{1g} orbital increases for both spins, whereas all e'_g bands go down (the total a_{1g} - e'_g splitting becomes 0.21 eV for $x=0.33$). This makes six e'_g Fermi surface hole pockets to disappear for small x values. Note, for all Na concentration LDA+ U predicts large a_{1g} pocket of Fermi surface centered around the Γ point in excellent agreement with ARPES spectra for $x < 0.7$. The additional electron pocket close to the Γ point appears in both LDA and LDA+ U methods for a large doping concentrations. It was discussed in our previous work^{23,24} in connection with the electronic theory for the itinerant magnetism of this compound.

Gutzwiller approximation. The free electron Hamiltonian for CoO_2 -plane in a hole representation is given by:

$$H_0 = - \sum_{\mathbf{f}, \alpha, \sigma} (\varepsilon^\alpha - \mu) n_{\mathbf{f}\alpha\sigma} - \sum_{\mathbf{f}, \mathbf{g}} \sum_{\alpha, \beta} t_{\mathbf{f}\mathbf{g}}^{\alpha\beta} d_{\mathbf{f}\alpha\sigma}^\dagger d_{\mathbf{g}\beta\sigma}. \quad (1)$$

where $d_{\mathbf{f}\alpha\sigma}$ ($d_{\mathbf{f}\alpha\sigma}^\dagger$) is the annihilation (creation) operator for the t_{2g} hole at Co site \mathbf{f} , spin σ and orbital index α , $n_{\mathbf{f}\alpha\sigma} = d_{\mathbf{f}\alpha\sigma}^\dagger d_{\mathbf{f}\alpha\sigma}$, and $t_{\mathbf{f}\mathbf{g}}^{\alpha\beta}$ is the hopping matrix element, ε^α is the single-electron energies, and μ is the chemical potential. All in-plane hoppings and single-electron energies were derived previously^{23,24} from the *ab-initio* LDA calculations. Since LDA-calculated hoppings and single-electron energies do not depend much on doping concentration, we used here parameters for $\text{Na}_{0.33}\text{CoO}_2$ from Table I of Ref.²⁴. To take bilayer splitting into account, we also consider here the hoppings $t_z^{\alpha\beta}$ between adjacent CoO_2 planes. Their values were also derived from LDA results and are equal to $t_z^{a_{1g}a_{1g}} = -0.0121$, $t_z^{e'_{g1}e'_{g1}} = 0.0080$, and $t_z^{e'_{g2}e'_{g2}} = -0.0086$.

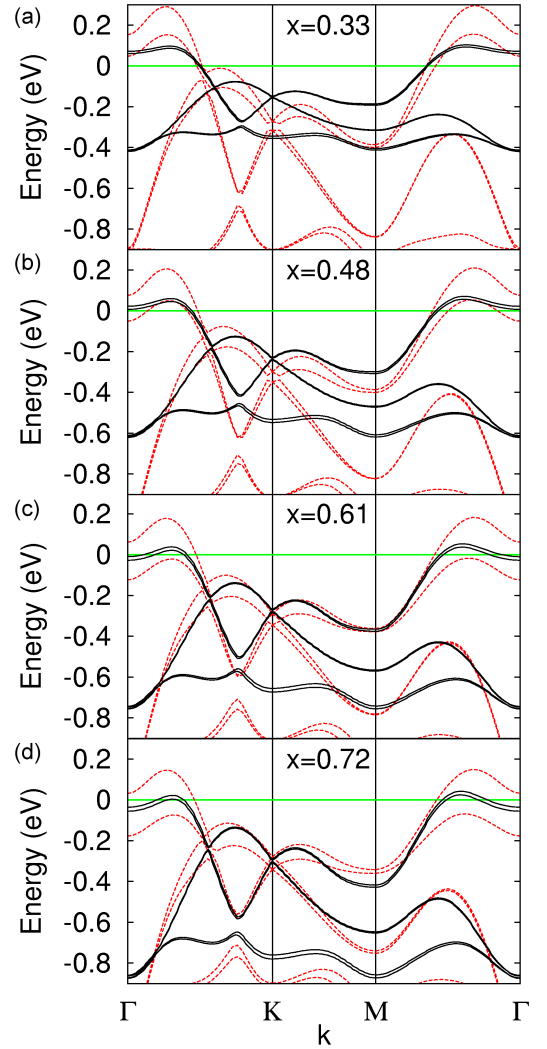


FIG. 2: (Color online) Band structure of Na_xCoO_2 for x equal to 0.33 (a), 0.48 (b), 0.61 (c), and 0.72 (d), obtained in LDA+ U is shown by the dashed (red) curves. Dispersion within the Gutzwiller approximation is shown by the solid (black) curves.

The Gutzwiller approximation^{25,26,27} for the Hubbard model provides a good description for the correlated metallic system. Its multiband generalization was formulated in Ref.²⁸. In this approach, the Hamiltonian describing the interacting system far from the metal-insulator transition for $U \gg W$, $J = 0$:

$$H = H_0 + \sum_{\mathbf{f}, \alpha} U_\alpha n_{\mathbf{f}\alpha\uparrow} n_{\mathbf{f}\alpha\downarrow}, \quad (2)$$

is replaced by the effective non-interacting Hamiltonian:

$$H_{eff} = - \sum_{\mathbf{f}, \alpha, \sigma} (\varepsilon^\alpha + \delta\varepsilon^{\alpha\sigma} - \mu) n_{\mathbf{f}\alpha\sigma} - \sum_{\mathbf{f} \neq \mathbf{g}} \sum_{\sigma} \sum_{\alpha, \beta} \tilde{t}_{\mathbf{f}\mathbf{g}}^{\alpha\beta} d_{\mathbf{f}\alpha\sigma}^\dagger d_{\mathbf{g}\beta\sigma} + C. \quad (3)$$

Here, $\tilde{t}_{\mathbf{fg}}^{\alpha\beta} = t_{\mathbf{fg}}^{\alpha\beta} \sqrt{q_{\alpha\sigma}} \sqrt{q_{\beta\sigma}}$ is the renormalized hopping between two lattice sites connected by the spatial vector $(\mathbf{f} - \mathbf{g})$, $q_{\alpha\sigma} = \frac{x}{1-n_{\alpha\sigma}}$, $n_{\alpha\sigma} = \langle \Psi_0 | n_{\mathbf{f}\alpha\sigma} | \Psi_0 \rangle \equiv \langle n_{\mathbf{f}\alpha\sigma} \rangle_0$ is the orbital's filling factors, $x = 1 - \sum_{\alpha\sigma} n_{\alpha\sigma}$ is the equation for the chemical potential. $\delta\varepsilon^{\alpha\sigma}$ are the Lagrange multipliers yielding the correlation induced shifts of the single-electron energies. The constant $C = \sum_{\alpha,\sigma} \delta\varepsilon^{\alpha\sigma} n_{\alpha\sigma}$ was determined from the condition that the ground state energy is the same for both Hamiltonians, $\langle \Psi_0 | H_{eff} | \Psi_0 \rangle = \langle \Psi_g | H | \Psi_g \rangle$, where $|\Psi_0\rangle$ is the wave function of the free electron system (3), and $|\Psi_g\rangle$ is the Gutzwiller wave function for the Hamiltonian (2). The Lagrange multipliers are determined by minimizing the energy $\langle \Psi_0 | H_{eff} | \Psi_0 \rangle$ with respect to the orbital filling factors $n_{\alpha\sigma}$. This results in the following expression for the single-electron energies renormalization:

$$\delta\varepsilon^{\alpha\sigma} = \frac{1}{2(1-n_{\alpha\sigma})} \sum_{\mathbf{f} \neq \mathbf{g}, \beta} \tilde{t}_{\mathbf{fg}}^{\alpha\beta} \langle d_{\mathbf{f}\alpha\sigma}^\dagger d_{\mathbf{g}\beta\sigma} \rangle_0. \quad (4)$$

It is this energy shift that forces the e'_g bands to sink below the Fermi energy²⁹. This is clearly seen in the doping-dependent evolution of the quasiparticle dispersion within Gutzwiller approximation in Fig. 2. To obtain these figures we solved self-consistently Eq. (4) and the equation on the chemical potential μ .

The comparison of the Gutzwiller approximation results with the LDA+ U dispersion reveals few very interesting conclusions. First, both approximations result in a suppression of e'_g hole pockets of the FS. Second, the bilayer splitting is strongly doping dependent and significantly reduced for Gutzwiller quasiparticles in comparison with the LDA+ U quasiparticles because the renormalization coefficient, $\sqrt{q_{\alpha\sigma}} \sqrt{q_{\beta\sigma}}$, occurs not only for the in-plane hoppings, but also for the interlayer hoppings $t_z^{\alpha\beta}$. Third, when both bonding and antibonding t_{2g} bands do not cross the Fermi level around the Γ point, the FS crossings are the same in both approximations (see Fig. 2a). It is the simple consequence of the Luttinger theorem which holds for both approaches. But for large x due to the larger bilayer splitting in LDA+ U the Fermi

surfaces become different, while the Luttinger theorem is still preserved. With increase of the doping concentration x the bandwidth of the Gutzwiller quasiparticles becomes closer to the LDA+ U ones because band renormalization factor $\sqrt{q_{\alpha\sigma}} \sqrt{q_{\beta\sigma}}$ comes closer to unity.

Dynamical Mean Field Theory (DMFT) calculations^{31,32} show that for the small U and non-zero J , e'_g FS pockets can be stabilized. On the other hand, DMFT calculations of Ref.³⁰ confirms results of the Gutzwiller approximation provided that U and the crystal field splitting are large.

Conclusion. In the present work employing *ab-initio* "constrained LDA" method we obtained Coulomb repulsion parameter $U=2.67$ eV for t_{2g} orbitals taking into account the screening by e_g -electrons in addition to the screening by itinerant s - and p -electrons. Hund's exchange parameter was found equal to $J=1.07$ eV.

Also, we have shown that due to the Co-O-Co bond angle close to 90° in Na_xCoO_2 the energy gap between LS and HS states is too large to be overcome by clusterization or reasonable distortions of crystal structure. Thus we conclude that realization of HS state is highly improbable in these particular substance.

Then, to analyze the effect of electronic correlations on the Fermi surface topology of Na_xCoO_2 we use two approaches, non-magnetic LDA+ U and Gutzwiller approximation for the Hubbard-type model based on the LDA band structure. Within LDA+ U the energy of the less occupied a_{1g} orbital increases for both spins, whereas all e'_g bands go down. This makes six e'_g FS hole pockets to disappear for small x values, in agreement with ARPES for $x < 0.7$. Gutzwiller approximation also resulted in a suppression of e'_g hole pockets at the FS. Moreover, the bilayer splitting was found to be strongly doping dependent and significantly reduced for Gutzwiller quasiparticles in comparison with LDA+ U quasiparticles.

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